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A Digest of

THE ENERGY OF FORMATION OF VACANCIES IN METALS AND ALLOYS

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When diffusion proceeds through the mechanism of vacancy motion the following relationship holds:

$$E_o = E_a + E_D \quad (1)$$

with E_o - activation energy of motion of volume diffusion, E_a - activation energy of motion of vacancies, and E_D - the energy of formation of vacancies.

For our purpose a grain boundary may be described as a localized high concentration of vacancies. Therefore, diffusion along grain boundaries does not require the energy of formation of vacancies:

$$E_{gr} = E_a \quad (2)$$

Substitution into equation 2 gives

$$E_o - E_{gr} = E_D, \quad (3)$$

that is the direct determination of E_D and E_o gives the possibility of determining E_a .

In reference 1) is presented a method for determining the number of vacancies and E_D from measurements of the thermal expansion coefficient at high temperatures. However, this method is not quite unambiguous.

Here we present a better method for determining the formation energy from the coefficient of thermal expansion.

It is assumed that (at equilibrium) due to heat motion there

exist vacancies in the lattice and that the atoms liberated in the formation of these vacancies occupy new lattice sites, so that the volume of the solid at high temperatures exhibits not only the influence of heat motion but of these new lattice sites as well.

We will assume further that the length of a sample obeying the aforementioned principles obeys the law:

$$l_t/l_o = A + BT + CT^2 + K \exp \left\{ - E_D/RT \right\} \quad (4)$$

where l_o is the original length, l_t - length at temperature t , A , B and C are constants, and K is equal to $1/3$ for cubic lattices. Using the data in the literature and eq. (4) we have determined the energy of formation of vacancies for a series of metals and alloys.

In table 2 are presented the data for the thermal expansion of aluminum, taken from ref. (5). In the first column are the temperature intervals, in the second the average expansion coefficient for this interval, in the third - the experimental l_t/l_o , assuming l_o to be the 0°K value. In the fourth column are given the values of l_t/l_o calculated from the formula $l_t/l_o = A + BT + CT^2$, in the fifth is

$$[(l_t/l_o)_{\text{exp}} - (l_t/l_o)_{\text{calc}}] = \Delta.$$

Finally in the last column is given E_D .

From table 2 we see that at temperatures higher than 300°C there appears a systematic deviation Δ , for which reason we have introduced the term $K \exp \left\{ - E_D/RT \right\}$. From reference (6) we see $(\Delta n/n) = \exp \left\{ - E_D/RT \right\}$ where Δn is the number of vacancies and n - the number of atoms. It is clear that

$$(\ell_t/\ell_o)^3 \exp -(\ell_t/\ell_o)^3 \text{ calc} = 3\Delta$$

$$3\Delta = \Delta n/n = \exp \left\{ -E_D/RT \right\} \quad (5)$$

Formula (5) was used to calculate E_D .

In tables 5, 6, and 7 are the expansion data, ref. 5, for Au, Ag, and Cu and the calculated energy of formation of vacancies.

If it is correct that the atoms liberated in the formation of vacancies occupy new sites, then the thermal expansion of the lattice as determined by the X-ray parameter " a "_t, should be given by the following relationship

$$a_t = A + BT + CT^2 \quad (6)$$

with A, B, and C are constants - the term $K \exp (-E_D/RT)$ not appearing in the lattice parameter.

In ref. 7 is given the measurements of the X-ray lattice parameter for Ag, Al, Au, and Cu, and in ref. 8 is given the same measurements for Cd together with calculations of the atomic volume of Cd at various temperatures.

In table 7 are presented the experimental data from ref. 7. The numbers have been taken from the figures since the authors do not present a table of the measurements.

In tables 8 and 9, are the values of Δa , the difference between the experimental value of the lattice parameter " a " and the value of " a " calculated from the formula (6).

For the sake of comparison we have calculated using the values of E_D for these elements given in table 1, the appropriate values of Δ to be expected in dilatometric measurements.

Although the X-ray measurements are of less accuracy than the dilatometric, it can be seen that the change in lattice parameter obeys eq. (6) but the change in length of a macroscopic sample obeys eq. (4).

There are no dilatometric measurements for Cd; therefore we have obtained $\Delta n/n$ from formula 3) and the data in table 1, where we see for Cd, $E_D = 5.6 \pm 1.2$ kcal/gm atom. In table 10 we present $\Delta n/n$ (1) corresponding to $E_D = 5.6$ and $\Delta n/n$ (2) calculated assuming $E_D = 6.8$ kcal/gm atom. In fig. 1, we see the comparison of the high temperature data of the lattice cell volume, v_{exp} , to the value, v_{calc} , calculated from $v_{calc} = A + BT + CT^2$.

According to refs. 9, 10, and 11, the energy of formation of vacancies may be determined from the change in the electrical resistivity of a sample upon quenching from high temperatures. For Au and Pt the authors⁽¹⁰⁾ obtain for E_D the values 18.2 and 27.7 kcal/gm atom respectively, and for Au⁽¹¹⁾ $E_D = 30$ kcal/gm atom.

The energy of formation of vacancies for Cu and Au has also been determined from the temperature dependence of the electrical resistivity at high temperatures obtaining $E_D = 20.7$ and 15.4 kcal/gm atom respectively. While this work has been criticized⁽¹³⁾, the criticism seems to us to be baseless, since it is shown in ref. 14) that the electrical resistivity of metals with anharmonic force law obey the law

$$\rho_t = A + BT + CT^2.$$

At high temperatures the vacancy term begins to play a role, $M \exp \{-E_D/RT\}$, since the vacancies possess an incremental resistivity.

We have also determined the energy of formation of vacancies from dilatometric data for several alloys: Pt + 20% Ir (15); Ni + 10% Cr (5); Ag, Ag + 10% Au, Ag + 20% Au, Ag + 40% Au, Ag + 60% Au, Ag + 80% Au and Au (all ref. 16).

The results of determinations by various methods are presented in table 11.

It will be necessary to have further experimental data and analysis to determine the applicability of each method of determining the energy of formation of vacancies.

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Table 1

Activation energies for self-diffusion E_o and grain boundary diffusion E_{gr} .

Material	E_o	E_{gr}	$\frac{E_{gr}}{E_o}$	Ref.
Cd	18.6	13.0	0.70	2
Zn	--	14.45	0.63	3
		$(E_{gr} = 63\% E_o)$		
Pb	25.7	15.7	0.61	4
Ag	45.9	20.2	0.44	5

Table 2

Mean dilatometric thermal expansion coefficient for aluminum versus temperature (ref. 5). The term $K \exp \left\{ - E_D / RT \right\}$ is assumed to become important for $T > 300^\circ\text{C}$.

$^\circ\text{C}$	$\alpha \cdot 10^6$	$\frac{l_t}{l_o} \text{ exp}$	$\frac{l_t}{l_o} \text{ calc}$	$\Delta \cdot 10^6$	$E_D \frac{\text{kcal}}{\text{gm atom}}$
0 - 50	23.66	1.001183	1.001188	- 5	.
0 - 100	.94	.002394	.002393	+ 1	
0 - 150	24.24	.003636	.003635	+ 1	
0 - 200	.56	.004912	.004913	- 1	
0 - 250	.91	.006228	.006228	0	
0 - 300	25.28	.007584	.007579	+ 6	
0 - 350	.68	.008988	.008968	+ 20	12,0
0 - 400	26.09	.010436	.010392	+ 44	11,9
0 - 450	.53	.011939	.011854	+ 85	12,2
0 - 500	27.00	.013500	.013351	+149	11,8
0 - 550	.48	.015114	.014886	+228	11,9
0 - 600	.99	.016794	.016457	+337	11,9

$$E_D = 11.95 \frac{\text{kcal}}{\text{gm atom}}$$

$$A = 0,994283$$

$$B = 1,9015 \cdot 10^{-5} \cdot T^{-1}$$

$$C = 7,313 \cdot 10^{-9} \cdot T^{-2}$$

Table 3

Δ 's from the thermal expansion coefficient of Al. Δ_1 uses $K \exp \{-E_D/RT\}$ for $T > 400^\circ\text{C}$, Δ_2 for $T > 500^\circ\text{C}$. (This table is only to show the mechanism and sensitivity of the method.)

$^\circ\text{C}$	$\Delta_1 \cdot 10^6$	$E_D \frac{\text{kcal}}{\text{gm atom}}$	$\Delta_2 \cdot 10^6$
50	+ 2		+198
100	+ 10		+123
150	+ 9		+104
200	+ 3		+ 57
250	- 5		+ 15
300	- 10		- 25
350	- 9		- 70
400	+ 3		-110
450	+ 18	14,0	-138
500	+ 67	13,0	-158
550	+120	12,9	-156
600	+189	12,9	-138

Table 4

Dilatometric determination of E_D for Au.

Au		
$^{\circ}\text{C}$	$\Delta \cdot 10^6$	$E_D \frac{\text{kcal}}{\text{gm atom}}$
50	- 18	
100	- 7	
150	- 4	
200	+ 1	
250	0	
300	+ 2	
350	0	
400	0	
450	+ 2	
500	+ 4	
550	+ 7	
600	+ 21	16,7
650	+ 31	17,1
700	+ 55	16,8
750	+ 75	17,1
800	+112	17,0
850	+154	17,2
900	+207	17,2
950	+266	17,3

$$E_D = 17,05 \frac{\text{kcal}}{\text{gm atom}},$$

$$A = 0,996456,$$

$$B = 1,2376 \cdot 10^{-5} \cdot T^{-1},$$

$$C = 2,641 \cdot 10^{-9} \cdot T^{-2}.$$

Table 5

Dilatometric determination of E_D for Ag

Ag		
$^{\circ}\text{C}$	$\Delta \cdot 10^6$	$E_D \frac{\text{kcal}}{\text{gm atom}}$
50	+ 6	
100	- 10	
150	+ 3	
200	+ 2	
250	0	
300	+ 4	
350	- 9	
400	- 5	
450	- 2	
500	+ 12	
550	+ 29	15,2
600	+ 59	15,0
650	+101	14,9
700	+154	14,8
750	+229	14,8
800	+312	14,8
850	+422	14,9
900	+548	14,9

$$E_D = 14,9 \frac{\text{kcal}}{\text{gm atom}},$$

$$A = 0,995044,$$

$$B = 1,7447 \cdot 10^{-5} \cdot T^{-1},$$

$$C = 2,949 \cdot 10^{-9} \cdot T^{-2}.$$

Dilatometer determination of E_D for Cu

Cu		
$^{\circ}\text{C}$	$\Delta \cdot 10^6$	$E_D \frac{\text{kcal}}{\text{gm atom}}$
50	- 10	
100	- 4	
150	- 1	
200	+ 1	
250	0	
300	+ 1	
350	0	
400	- 3	
450	- 2	
500	+ 5	
550	+ 11	
600	+ 18	17,0
650	+ 33	17,0
700	+ 49	17,0
750	+ 75	17,1
800	+103	17,2
850	+143	17,7
900	+186	17,4
950	+234	17,7
1000	+295	17,7

$$A = 0,995773; B = 1,46515 \cdot 10^{-5} \cdot T^{-1}; C = 3,448 \cdot 10^{-9} \cdot T^{-2};$$

$$E_D = 17,3 \frac{\text{kcal}}{\text{gm atom}}$$

Table 7

X-ray lattice parameter "a" vs. temperature (ref. 7).

$^{\circ}\text{C}$	Au Å	Ag Å	Cu Å	Al Å
50	4.0723	4.0800	3.6100	4.0434
100	4.0753	4.0835	3.6135	4.0484
150	4.0783	4.0883	3.6170	4.0533
200	4.0815	4.0927	3.6205	4.0580
250	4.0845	4.0970	3.6238	4.0640
300	4.0876	4.1010	3.6274	4.0700
350	4.0913	4.1052	3.6313	4.0762
400	4.0940	4.1097	3.6345	4.0826
450	4.0972	4.1140	3.6385	4.0893
500	4.1011	4.1183	3.6420	4.0965
550	4.1038	4.1235	3.6460	4.1039
600	4.1073	4.1285	3.6500	4.1110
650	4.1110	4.1333	3.6537	4.1150 (625 $^{\circ}\text{C}$)
700	4.1150	4.1387	3.6580	
750	4.1180	4.1440	3.6620	
800	4.1220	4.1493	3.6658	
850	4.1260	4.1549	3.6703	
900	4.1295	4.1606	3.6743	
950	4.1335	--	3.6790	
1000	4.1378	--	3.6838	
1050	4.1420	--	--	

Table 8

Deviations of " a_{exp} " from " a_{calc} " using eq. 6) for Cu and Au.

t $^{\circ}\text{C}$	Cu			Au		
	$\Delta a \cdot 10^4 \cdot \text{\AA}$	$\frac{\Delta a}{a} \cdot 10^2 \%$	$\Delta \cdot 10^2 \%$	$\Delta a \cdot 10^4 \cdot \text{\AA}$	$\frac{\Delta a}{a} \cdot 10^2 \%$	$\Delta \cdot 10^2 \%$
50	-16	-4,4		-33	- 8	
100	-11	-3,0		-17	- 4	
150	- 4	-1,1		- 3	-0,7	
200	- 3	-0,8		- 7	-1,7	
250	- 3	-0,8		- 5	-1,2	
300	- 1	-0,3		- 2	-0,5	
350	+ 3	+0,8		+ 5	+1,2	
400	0	0		+ 2	+0,5	
450	+ 4	+1,1		+ 2	+0,5	
500	+ 2	+0,6		+ 9	+2,2	
550	+ 4	+1,1		+ 3	+0,7	
600	+ 5	+1,4		+ 3	+0,7	
650	+ 2	+0,6		+ 5	+1,2	
700	+ 3	+0,8		- 2	-0,5	
750	+ 5	+1,4		+ 1	+0,2	+0,8
800	0	0	+0,6	+ 2	+0,5	+1,2
850	+ 1	+0,3	+0,9	+ 3	+0,7	+1,7
900	- 3	-0,8	+1,2	- 3	-0,7	+2,4
950	- 3	-0,8	+1,7	- 4	-1,0	+3,1
1000	+ 1	+0,3	+2,2	+ 4	-1,0	+4,0
1050				- 6	-1,4	+5,3

$$A = 3,5941 \text{\AA},$$

$$B = 4,853 \cdot 10^{-50} \text{\AA} \cdot T^{-1},$$

$$C = 1,71 \cdot 10^{-80} \text{\AA} \cdot T^{-2}.$$

$$A = 4,0612 \text{\AA},$$

$$B = 3,5 \cdot 10^{-50} \text{\AA} \cdot T^{-1},$$

$$C = 2,0 \cdot 10^{-80} \text{\AA} \cdot T^{-2}.$$

Table 9

Deviations of " a_{exp} " from " a_{calc} " using eq. 6) for Ag and Al.

$^{\circ}\text{C}$	Ag			Al		
	$\Delta a \cdot 10^4 \cdot \text{\AA}$	$\frac{\Delta a}{a} \cdot 10^2 \%$	$\Delta \cdot 10^2 \%$	$\Delta a \cdot 10^4 \cdot \text{\AA}$	$\frac{\Delta a}{a} \cdot 10^2 \%$	$\Delta \cdot 10^2 \%$
50	-23	-5,6		-5	-1,2	
100	-21	-5,1		0	0	
150	-9	-2,2		0	0	
200	-1	-0,2		-5	-1,2	
250	+3	+0,7		0	0	
300	+2	+0,5		+2	+0,5	
350	+3	+0,5		+2	+0,5	
400	+5	+1,2		+1	+0,2	+0,5
450	+3	+0,7		0	0	+0,9
500	-1	-0,2		0	0	+1,6
550	+3	+0,7		0	0	+2,6
600	+3	+0,7		-5	-1,2	+3,9
650	0	0		-7 (625 $^{\circ}\text{C}$)	-1,7	+4,7
700	+1	+0,2	+0,9			
750	0	0	+1,3			
800	-4	-1,0	+1,8			
850	-6	-1,4	+2,5			
900	0	0	+3,3			

$$A = 4,0645 \text{\AA},$$

$$B = 4,457 \cdot 10^{-5} \text{\AA} \cdot T^{-1},$$

$$C = 3,25 \cdot 10^{-8} \text{\AA} \cdot T^{-2}.$$

$$A = 4,0223 \text{\AA}$$

$$B = 4,58 \cdot 10^{-5} \text{\AA} \cdot T^{-1},$$

$$C = 6,48 \cdot 10^{-8} \text{\AA} \cdot T^{-2}.$$

Table 10

Lattice cell volume of Cd calculated using $E_D = 5.6$ kcal/gm atom compared to the X-ray determination.

$^{\circ}\text{C}$	v_{exp} $\text{\AA}^3$	v_{calc} $\text{\AA}^3$	$\Delta v \cdot 10^3$ $\text{\AA}^3$	$\frac{\Delta v}{v} \cdot 10^2 \%$	$\frac{\Delta n}{n}(1) \cdot 10^2 \%$	$\frac{\Delta n}{n}(2) \cdot 10^2 \%$
49	21.515	21.512	+ 3	+1,4		
72	.567	.569	- 2	-0,9		
85	.587	.587	0	0		
100	.626	.619	+ 7	+3,2		
106	.632	.632	0	0		
109	.632	.638	- 6	-2,8		
123	.665	.669	- 4	-1,8		
127	.686	.678	+ 8	+3,7		
155	.740	.741	- 1	-0,5		
176	.774	.789	-15	-6,9		
187	.809	.816	- 7	-3,2	+21,4	+ 5,7
208	.874	.866	+ 8	+3,7	+27,6	+ 7,9
229	.904	.918	-14	-6,5	+35,5	+ 11
254	.974	.980	- 6	-2,7	+45,8	+15,2
263	22.012	22.003	+ 9	+4,1	+50,0	+16,6
279	.050	.044	+ 6	+2,7	+60,3	+19,8

$$A = 20,983 \text{\AA}, B = 1,25 \cdot 10^{-3} \text{\AA}^3 \cdot \text{T}^{-1}, C = 1,2187 \cdot 10^{-6} \text{\AA}^3 \cdot \text{T}^{-2}.$$

Table 11

The energy of formation of vacancies in various materials as determined by various methods.

Materials	Dilatometric	High Temperature Resistivity	Quenching
Au	17,1; 16,7	15,4	18,2; 29,5
Cu	17,3; 19,5	20,7	--
Ag	14,9; 16,9	--	--
Al	11,95; 11,4	--	--
Pt	--	--	27,2
Pt + 20% Ir	28,0	--	--
Ni + 10% Cr	19,4	--	--
Ag	16,9	--	--
Ag + 10% Au	17,4		
Ag + 20% Au	17,1		
Ag + 40% Au	15,2		
Ag + 60% Au	16,2		
Ag + 80% Au	18,9		
Au	16,7		

